THE PREPARATION AND POLYMERIZATION OF SOME UNSATURATED ISOCYANATES

By

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CHAPTER I

INTRODUCTION

A. History of Isocyanate Chemistry

The first synthesis of an isocyanate was reported by Wurtz[1] in 1849 in a paper which also disclosed reactions of the compound with water, amines and alcohols as well as its formation of dimers and trimers.[2]

Much of the chemistry of organic isocyanates was known before 1910, and many of the classical reactions of these compounds were discussed in publications during the period 1890-1920.[3,4] In subsequent years, isocyanates were not entirely neglected, and numerous references to both synthesis and reactions can be found in the literature.[5] It was not until World War II that isocyanate chemistry came into its own when commercial exploitation and modification by the Germans led to an almost universal desire to utilize these compounds.[4] The significant progress which has occurred in the field since that time has been carried on primarily through the efforts of industrial research.

The voluminous formal and patent literature published from 1940 to this time is an index of the scope and intensity of research in the realm of isocyanate chemistry, and the detailed variations are so numerous that a complete discussion is not warranted. However, reviews[5,6] are available which treat the chemistry of these materials in considerable detail.

B. Organic Isocyanates as Related to Polymer Chemistry

Tremendous progress has been made in the fields of polymers and polymer modification, and intensive study of isocyanate chemistry began when its potential importance in these areas was recognized.[2,5]

Most, if not all, of the polymer applications of isocyanates rely to a large extent upon the characteristic high reactivity of the -NCO group with compounds that contain an active hydrogen. Isocyanates react with amines, amides, alcohols, phenols, water, carboxylic acids, thiols and active methylene groups. It should be noted that only polyfunctional isocyanates, diisocyanates in particular, have attained commercial significance, and technological effort has been stimulated only by the development of those which are especially adapted to polymer synthesis as a consequence of their reactivity.[5,7]

When an isocyanate is caused to react with a compound that is monomeric in nature and contains only one reactive hydrogen-containing group, a simple condensation or addition product is generally formed. If the two reactants are bifunctional, the product is polymeric, and if compounds with more than two hydrogen-containing groups are reacted with diisocyanates, high-molecular-weight polymers of cross-linked structure are obtained.[4]

The reaction of di- or polyfunctional isocyanates with reagents such as water, amines and alcohols is generally comparable to their monofunctional counterparts. No abnormal reactivity in polymeric systems has been reported, and the reaction rates observed have been independent of the polymeric series participating.[5] Because of the high reactivity of isocyanates, their reactions are rarely devoid of undesirable side reactions. For this reason, reactions involving synthesis of high-molecular-weight products are somewhat difficult to control and reproduce. In this latter respect, isocyanate reactions do not differ markedly from other condensation systems.

The chemistry of urethane polymers is closely associated with that of polyisocyanates and polyfunctional active hydrogen compounds from which they are made.[7] In recent years, this complex branch of chemistry has received considerable attention, and as a result the understanding of isocyanate chemistry has greatly improved.

Low-molecular-weight or highly crystalline higher-molecular-weight difunctional alcohols, amines, carboxylic acids, and polyfunctional reagents form, with di- and polyisocyanates, the basis for plastics, coatings, films and fibers.[5] Such polymers are of interest because of their tensile strength, low water absorption, good insulating properties and good resistance to outdoor exposure.

Polyisocyanates, because of their compatibility and reactivity with a variety of materials, have been used in numerous adhesive applications.[2,5,8,9] Examples are the cross-linking of polymers in obtaining adhesion to heretofore difficult-to-adhere-to substrata.[4]

Aromatic and aliphatic isocyanates have also been used in polymerizations relative to the formation of elastomers.[5] The basic intermediates employed are relatively high-molecular-weight, linear, low-melting glycols which include polyester and polyether glycols of molecular weights of 1,000 or greater. Curing of the raw polymers to form finished elastomeric articles can be effected by heating the initial reaction product in the presence of added polyisocyanate.

Isocyanates, in their reactions with water and carboxylic acids, produce carbon dioxide as a by-product. As a consequence, the polymerizing material is blown up to form a voluminous, porous structure. When this phenomenon

is properly controlled, foams with excellent structure and almost any desired density can be obtained.[4,5,10] Foam "prepolymers" are reaction products of di- or polyisocyanates with the same intermediates as used in the formation of bulk elastomers and plastics, with the difference that excess isocyanate is used and a low-molecular-weight, viscous fluid is formed. Addition of the final reactant (water or carboxylic acid) is made just prior to use. The mixture is poured into a mold, and chain extension, cross-linking and foaming occur simultaneously. The use of materials of this sort has opened a new field for isocyanate chemistry. Such polymers are used as cushioning for furniture (flexible foams) and insulating liners for refrigerators (rigid foams).[10]

The above mentioned major areas in which isocyanates are today finding popular application have been thoroughly discussed and schematically outlined in a review by Arnold, Nelson and Verbanc.[2]

Another general reaction of isocyanates is that which takes place with compounds that do not contain active hydrogen.[10] Taub and Mc.Ginn [11] have reviewed the chemistry of the polymerization of isocyanates. Under the influence of tertiary amines, aromatic isocyanates dimerize to yield 1,3-substituted uretidinediones, while in the presence of alkalies or carboxylates, both aliphatic and aromatic

isocyanates trimerize to form tri-N-substituted isocyanurates. More recently, it was reported[12] that isocyanates may be polymerized at low temperatures to form N-substituted-1-nylons. An example of this may be the reaction of phenyl isocyanate at -40° to yield poly(phenyl isocyanate), a white solid insoluble in N,N-dimethylformamide and benzene.[13] The formulas of 1,3-substituted uretidinediones, tri-N-substituted isocyanurates and N-substituted-1-nylons are given in the following chapter.

There have also been disclosed, although references to them in the literature are scarce, a few products which involve simultaneous reactions of not only isocyanate functions but other types of functional groups as well. In one example[5,14] a monoisocyanate bearing a carboxyl group is condensed with a diaminoalcohol to yield a fiber-forming polymer.

Intermediates, resulting from isocyanate reactions, that contain polymerizable olefinic structures have also been reported. Thus, monomeric dihydroxy esters of the type $HOR'O_2CRCO_2R'OH$, where either R or R' is alkylene, are caused to react with diisocyanates, and the resulting urethane polymers are copolymerized with styrene.[15] Also, unsaturated ethers which were obtained by reaction of a diisocyanate with an aminoalkyl vinyl ether have been copolymerized with methyl methacrylate;[16] and poly(substituted

ureas) resulting from the reaction of alkoxyalkyl isocyanates with 2-aminoethyl vinyl ether and subsequent polymerization have been used to modify urea-formaldehyde films.[17]

C. Development of the Problem

In 1944, a material believed to be an impure sample of poly(vinyl isocyanate) and/or copolymer of vinyl isocyanate and acrylyl chloride was first reported.[18] This substance was formed during an attempted preparation of polvinylamine and was only partially or sparingly soluble in N,N-dimethylformamide.

In a 1950 patent[19] it was suggested that copolymers of a 1-alkenyl isocyanate, e.g., vinyl isocyanate, and vinyl or vinylidene compounds might be prepared. The incorporation of the isocyanate group would permit further modification of the product through reaction with monomeric or polymeric compounds containing one or more reactive hydrogen atoms. This particular patent dealt with modified unsaturated alkyd resins in which unesterified carboxyl and hydroxyl groups of the resin, as initially prepared, had been caused to react with the -NCO grouping of an isocyanate which also contained a polymerizably reactive olefinic radical. It was postulated that the modified alkyd resin might undergo polymerization and copolymerization reactions through the unsaturated hydro-

carbon radicals of the isocyanate as well as through the double bonds within the alkyd resin itself. Another example utilizes mono- or polyisocyanates which contain ethylenic bonds and which may be polymerized under such conditions that chain extension through reaction of both types of functions occurs simultaneously.[5,20]

During the years 1955-57, some work was carried out concerning the copolymerization of isocyanatoalkyl vinyl ethers with vinylidene compounds to give materials which were said to be valuable as coatings, adhesives, textile finishing agents and wool stabilizers.[21,22] Also, in 1957, a report[23] was made of the copolymerization of ethyl methacrylate isocyanate with methyl methacrylate in xylene using free radical initiation. The result was a highly viscous solution which formed a gel upon addition of ethylenediamine or tris(hydroxymethyl) propane. There was no mention made of isolating the linear polymer however.

The synthesis of polyisocyanatopolystyrene has been reported.[24] This was performed by causing phosgene to react with polyaminostyrene. The author states that the resulting materials "are valuable for 'tailor-made' resins." The polymer itself has been incorporated into a new method for linking enzymes to solid structures.[25]

Iwakura, Sato, Tamikado and Mizoguchi,[26] Hart[27] and others[28] have carried out low conversion copolymerizations

of vinyl isocyanate as well as reactions of vinyl and isopropenyl isocyanates with ammonia and amines to yield unsaturated ureas which were then polymerized to low-molecular-weight products. Iwakura, Sato and Munakata[29] report the synthesis of α-phenylvinyl isocyanate which, on standing, polymerized to a viscous oil and then to a solid.

Most recently, Sato[30] has stated that

> 1-alkenyl isocyanates . . . are very interesting materials in organic chemistry, especially in polymer chemistry, because these compounds seem to give high-molecular-weight substances by polymerization and copolymerization, and the polymers obtained are able to bring about further polymer reactions. But the preparation and properties of these compounds have not been investigated systematically in spite of many papers.

These thoughts might also apply to isocyanates possessing olefinic groups at positions other than α , β to the -NCO function, and it is believed that such properties regarding unsaturated isocyanates are worthy of further study.

CHAPTER II

DISCUSSION I

A. Statement of the Problem

The purposes of this research are: 1) to study the preparation of heterofunctional monomers having the structure, CH_2=CH-R-NCO; 2) to prepare derivatives of these monomers by causing the -NCO groups to react with active hydrogen-containing compounds; 3) to investigate the polymerization and/or copolymerization of the unsaturated monomers to produce polymers that contain the reactive isocyanate group;* 4) to characterize the resulting polymers as to solubilities, melt temperatures, intrinsic viscosities and infrared spectra, and 5) to study the reactions of said polymers with mono- and difunctional active hydrogen compounds to form, respectively, linear and cross-linked polyurethanes and polyureas.

The succeeding discussion is intended to relate the reactions and properties of isocyanates and the

*Polymerization may be represented as:

$$n\ CH_2 = CH\text{-}R\text{-}NCO \longrightarrow \left[CH_2\text{-}CH(R\text{-}NCO) \right]_n$$

polymerization of unsaturated monomers to the problem at hand. Specific phenomena, both desirable and undesirable, are considered.

B. Synthesis of Isocyanates

Numerous methods for the preparation of organic isocyanates have been developed based on such diverse reactions as the Lossen[31,32] and Curtius[33] rearrangements, double decomposition between a cyanate salt and an ester of an inorganic acid,[34,35] thermal decomposition of ureas[36] and urethanes[37] and the phosgenation of amines.[2,3,14]

While the phosgenation of amines (equations 1 and 2) is generally selected for large scale manufacture of isocyanates, the Curtius rearrangement (equation 3) seems to be the most useful laboratory method.

$$RNH_2 + COCl_2 \longrightarrow RNHCOCl + HCl \qquad (1)$$

$$RNHCOCl \xrightarrow{130\text{-}300^\circ} RNCO + HCl \qquad (2)$$

$$RCON_3 \xrightarrow{60\text{-}100^\circ} RNCO + N_2 \qquad (3)$$

The immediate availability of the starting materials, undecylenic acid (Matheson, Coleman and Bell), β-allyloxypropanoic acid (this laboratory) and acrylic acid (Eastman), precluded any decision as to which compounds should be studied. The acyl azides could be prepared from the

corresponding acyl halides and caused to rearrange to yield the desired isocyanates.

C. Reactivity, Reactions and Properties of Organic Isocyanates

The electronic configuration of the isocyanate group can be represented as follows:[5,7]

$$\underset{(+)(-)}{R\text{-}N{=}C\text{-}O} \longleftrightarrow R\text{-}N{=}C{=}O \longleftrightarrow \underset{(-)(+)}{R\text{-}N\text{-}C{=}O}.$$

(I) (II)

Because of the greater electron-attracting properties of oxygen as compared to nitrogen, structure (I) is more nearly representative of the chemical behavior of these compounds than is structure (II).[5,7] Electron density is greatest on the oxygen (highest net negative charge) and least on the carbon (highest net positive charge). The nitrogen atom is intermediate with a net negative charge.

It should be noted that the reactivity of an isocyanate depends on its type and can best be understood by considering the above electronic structure. The reactions of isocyanates with active hydrogen-containing compounds involve attack by a nucleophilic center upon the electrophilic carbon of the isocyanate. Therefore, if steric factors are neglected, any electron-withdrawing

group attached to the -NCO moiety should increase the positive charge on the carbon atom, thereby increasing the reactivity towards nucleophilic attack. Conversely, electron-donating groups should reduce the reactivity of the isocyanate. A representative series of the decreasing reactivity of isocyanates is:[3]

$$ArNCO > RCH_2NCO > RR'CHNCO > RR'R''CNCO$$

Indeed, the reaction rates of negatively substituted aromatic isocyanates have been reported $10^5 - 10^6$ times as great as those for alkyl derivatives.[2] Furthermore, recent studies[38] have shown that 1-alkenyl isocyanates, with a carbon-carbon double bond conjugated to the -NCO group, have greater reactivity than ethyl and other unsaturated isocyanates without such conjugation, and steric effects, provided by substitution in the α-position, also affect reactivity. Thus, the compounds chosen for study represent different degrees of reactivity and should provide interesting results both in monomer reactions and when incorporated into a polymer chain.

Just as the reactivity of the isocyanate group increases as the electrophilic nature of its carbon increases, so the reactivity of the agent attacking the electrophilic carbon will increase as its nucleophilicity increases.[5] Thus,

$$RNH_2 > PhNH_2 > ROH > PhOH > RSH$$

Consideration of the above factors in most cases makes it possible to predict, on a qualitative basis, the relative reactivity of various isocyanates with compounds that contain active hydrogen. In general, all compounds that contain a hydrogen atom attached to nitrogen will react as follows:[3]

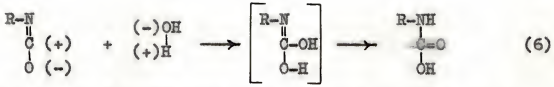
$$RNCO + HN< \longrightarrow RNHCON< \qquad (4)$$

For example, amines give ureas, amides give acyl ureas and ureas give biurets. Amines generally react much faster than amides or ureas. Primary alcohols react spontaneously with the formation of a urethane.[3]

$$RNCO + R'OH \longrightarrow RNHCOOR' \qquad (5)$$

Secondary and tertiary alcohols react more slowly, but the reaction can be catalyzed.

Isocyanates react with water at ordinary temperatures. In many cases, the reaction is violent and instantaneous but in others reaction occurs only if a catalyst is present.[7] As in other reactions between a compound containing active hydrogen and an isocyanate, the nucleophilic center of the water molecule attacks the electrophilic carbon of the isocyanate, while the proton goes to the negative oxygen atom. This intermediate then rearranges to give a more stable configuration as follows:[7]



(6)

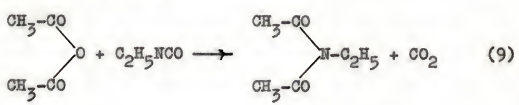
The unstable N-substituted carbamic acid reacts further, and the amine is believed to be a second intermediate.

$$RNHCOOH \longrightarrow RNH_2 + CO_2 \qquad (7)$$

$$RNH_2 + RNCO \longrightarrow (RNH)_2CO \qquad (8)$$

Thus, isocyanates are hydrolyzed by water, and the end product may be a urea, an amine or a mixture of the two. In addition, the direct synthesis of triarylbiurets by reaction of aromatic isocyanates with water has been reported.[5] It is this ease of hydrolysis which necessitates considerable care in handling isocyanates, including protection from moisture normally present in the atmosphere, in order to assure high purity both during preparation and storage.

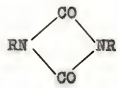
In 1894, Wurtz[39] prepared N-ethyldiacetamide by condensing acetic anhydride with ethyl isocyanate at 82-88° according to equation 9.[10]



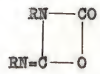
(9)

More recently, Hurd and Prapas[40] extended this reaction to atomatic anhydrides by preparing N-phenylphthalimide from phthalic anhydride and phenyl isocyanate.

As mentioned in Chapter I, polymerization is another general reaction of isocyanates and one which at times can be undesirable. The mechanisms of dimerization and trimerization are not well understood. In some cases, it is said that isocyanate dimerization is an equilibrium reaction and that the conversion to dimer increases with decreasing temperature.[5] In other cases such polymerizations are brought about by heating.[3] The symmetrical structure (III) was originally assigned to the dimer, but an alternative (IV) has been postulated and some support presented.[35]

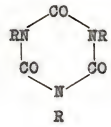


(III)



(IV)

Crystallographic and infrared studies support structure (III) for the solid material.[41] The structure of isocyanate trimers is believed to be a trisubstituted isocyanurate:



The general reaction typical of isocyanate polymerization is as follows:[10]

$$nR\text{-}NCO \longrightarrow \left(\begin{matrix} R & O \\ | & \| \\ N & -C \end{matrix}\right)_n \quad . \tag{10}$$

The catalysis of isocyanate reactions by tertiary amines is believed to occur as a result of increased polarization of the C=O bond.[42,43] The possible mechanism of such a base catalysis includes activation of the isocyanate through the formation of a "base-isocyanate complex" which may be formed by a direct attack on the isocyanate by the base.[44,45]

$$R_3N: + R'NCO \longrightarrow R'N{=}\overset{\overset{NR_3}{(+)}}{C}{-}O\ (-) \tag{11}$$

The high reactivity of isocyanates makes certain precautions essential in handling and using these chemicals. Contact with the skin and eyes and breathing of the vapors should be avoided. Isocyanates of low molecular weight (less than six carbons) are lachrymators and may give rise to increased physical difficulties with asthmatic subjects.[3] The aliphatic isocyanates are generally more toxic than the aromatics, and the toxicity of aliphatics having less than eight carbons in the chain is said to be very high.[4] A complete review of the hazards of isocyanates has been made by Zapp.[46]

D. Determination and Identification of Isocyanates

A well-known method for determining the amount of isocyanate present in a mixture is the addition of excess n-butylamine to a weighed sample and back titration with dilute sulfuric acid to the methyl-red end point.[47] Stagg[48] has developed methods for determining the purity of commercial grade isocyanates based on gravimetric as well as volumetric techniques.

The intense absorption of infrared radiation at the wavelength of 4.4 microns caused by the isocyanate group in a molecule is also an excellent means for determining its presence. This characteristic absorption has even been used for plotting the course of reactions.[49] Results[50] have shown that the -NCO function gives an extremely intense absorption at 2269±6 cm.$^{-1}$ and unlike the absorption caused by -CN, that of -NCO is apparently unaffected by adjacent unsaturation. The isocyanate stretching absorption bands of various 1-alkenyl isocyanates are reported to all appear between 2266 cm.$^{-1}$ and 2256 cm.$^{-1}$.[30]

Elemental analysis is a standard technique for proving the purity of a compound and, as applied to this work, may also be used for determining the amount of isocyanate functionality present in a given polymer.

E. Spectrophotometric Studies

Reaction products of isocyanates with compounds that contain active hydrogen give rise to infrared absorption characteristic of amide functions, i.e., $\left(\text{N-C}\right)$. Although a number of papers concerned with the spectra of urea and urethane derivatives have been presented, it is not possible to interpret fully the intricacies of the results, and there are different opinions for the assignment of the amide band II. However, all urea derivatives have the amide band I arising from the carbonyl group, and those which possess at least one hydrogen at the nitrogen atom have the amide band II arising from NH deformation.[30]

Boivin and Boivin[51] have measured the infrared spectra of the types, $CH_3NHCONHR$, and found the amide band I at 1660-1620 cm.$^{-1}$ and amide band II at 1630-1580 cm.$^{-1}$. Sato[30] has studied compounds of the type $RCH{=}C(R')\text{-}NHCO\text{-}NHC_4H_9$ and has found that all had amide band II in the region 1583-1555 cm.$^{-1}$ and a different band near amide band I. N-vinyl-N'butylurea had strong bands at 1666 cm.$^{-1}$ and 1638 cm.$^{-1}$.

Moelants and Hart[52] have made an intensive study of 1-alkenyl ureas in the infrared region, 3000-2900 cm.$^{-1}$. These same authors give amide II absorptions between 1640 cm.$^{-1}$ and 1600 cm.$^{-1}$ as being due to vibrations of

$-CONH_2$ and between 1615 cm.$^{-1}$ and 1555 cm.$^{-1}$ caused by vibrations of -CONH-.

The spectra of dimeric isocyanates exhibit carbonyl absorptions in the regions of 1773 cm.$^{-1}$ and 1756 cm.$^{-1}$, while trisubstituted isocyanurates have shown a single C=O absorption in the region between 1711 cm.$^{-1}$ and 1694 cm.$^{-1}$.[35]

Infrared absorption spectra have proven to be very useful in identifying chemical groups within a polymer. In addition polymerization of unsaturated compounds it is of some importance to note whether any residual unsaturation is present in the product.

All stretching vibrations involving the carbon-carbon double bond, for which there is a change in dipole moment, cause absorptions in the 1645 cm.$^{-1}$ region. More detailed information can be obtained, however, by examining the C=C-H hydrogen deformation absorptions at 1000-800 cm.$^{-1}$.[33] The vinyl type in olefins is characterized by two frequencies, namely, in the area of 990 cm.$^{-1}$ and in the area of 910 cm.$^{-1}$. The first is attributed to =CH- and the second to the CH_2= group.[52]

Infrared spectra of copolymers exhibit absorptions that are characteristic of each monomer used. Some of the groups expected to be present in copolymers prepared in this investigation are given, with their characteristic frequencies (in wave numbers), in Table 1.[35,52,53,54]

F. Techniques of Vinyl Polymerization

The polymerization of unsaturated monomers is a typical chain reaction and can be initiated by a variety of methods.[53] The four types of initiators to which vinyl monomers respond are: 1) free radical; 2) cationic; 3) anionic; and 4) coordination.[55]

Probably the most general method of initiation depends upon the generation of free radicals, and there are several techniques available (e.g., thermal, ultraviolet light). In most cases, it is necessary to add, in small proportions, an agent that will generate free radicals in situ. There are a number of compounds of this nature which are popular and may be obtained commercially.[55] While it is claimed occasionally that a certain free radical initiator has inherent advantages, this is something which, for the most part, is learned only by trial and error. Only two initiators will be used in this study, namely, dibenzoyl peroxide and α, α'-azodiisobutyronitrile.

Bulk polymerization is a useful technique for converting monomer to polymer because of its simplicity. In this method catalyst is added to undiluted monomer and the mixture is carried through the polymerization cycle. In order to obviate some of the difficulties encountered with bulk polymerization, such as overheating and formation

of local hot spots, solution polymerization has been used to some extent.[55] Suspension and emulsion polymerization techniques are also known, but since water is normally used as a carrier, these are not applicable to the polymerization of isocyanates for obvious reasons.

The largest single factor in determining whether a polymerization is successful or not is the quality of the monomers. It is absolutely essential that the starting materials be pure.[55]

There are a number of standard texts which treat the problems relative to polymer chemistry, both theoretical and practical, in a detailed manner.[53,55,56,57]

TABLE 1

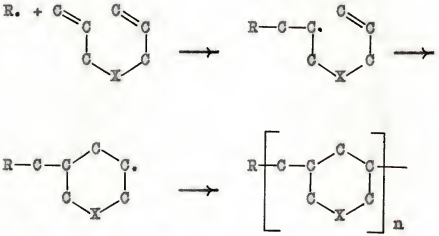
CHARACTERISTIC ABSORPTIONS OF SOME ORGANIC FUNCTIONS

Function	Absorption Frequency ($cm.^{-1}$)
Amide	3320, 1680-1660, 1630-1550
Anhydride	1750
Aromatic	1620, 1490, 770-742
Ester	1730
Isocyanate	2266-2256
Isocyanate Dimer	1773-1756
Isocyanate Trimer	1711-1694

CHAPTER III

DISCUSSION II

It is possible for certain structurally favorable unconjugated dienes to polymerize according to the following equation:[55]

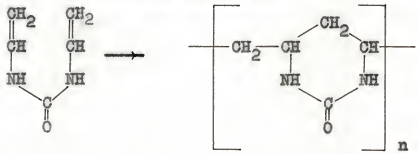


(12)

where X = C, O, S, N, Si, P.

Polymerizations of this type were first reported by Butler and Angelo[58] and soon thereafter by Marvel and Vest[59] and Jones.[60] Since that time, much evidence has been accumulated in support of such an alternating intramolecular-intermolecular chain propagation mechanism.[61,62,63,64]

On the basis of this knowledge, one might predict that the expected product of the reaction of vinyl isocyanate with water, namely N,N'-divinylurea, is theoretically capable of undergoing polymerization and/or copolymerization by the same mechanism.



(13)

The investigation of such a possibility has been undertaken.

It should be noted that the problem proposed for study is one with obvious difficulties. Although N,N'-divinylurea has not been reported, several papers concerning the properties of similar 1-alkenyl ureas have been published.[27,30,52] In each case it has been found that the instability of such compounds is quite high. The instability supposedly arises from the existence of tautomerism within these molecules. In the case of N,N'-divinylurea, such tautomerism may be exemplified as:

(V) (VI) (14)

The diethylidene urea, represented by structure (VI), may be quite susceptible to hydrolysis.

CHAPTER IV

EXPERIMENTAL

A. Equipment and Data

All temperatures herein are uncorrected and reported in degrees Centigrade. Pressures are expressed in millimeters of mercury, having been determined by means of a Zimmerli gauge.

Refractive indices were obtained with a Bausch and Lomb Abbe 34 refractometer fitted with an achromatic compensating prism.

Infrared spectra were obtained on either a Perkin-Elmer Infracord or a Perkin-Elmer Model 21 spectrophotometer.

Ultraviolet radiation was supplied by a Blak-Ray long-wave ultraviolet lamp, model XX-15.

Melting point determinations of monomeric compounds were carried out in open capillary tubes in an electrically heated block, while those of polymeric materials were performed on a Kofler micro hot-stage and viewed through a Unitron polarizing microscope.

Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde semi-micro dilution viscometer set in a constant temperature bath.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

B. Synthesis of Monomers

1. Purification of Thionyl Chloride

Thionyl chloride, as obtained from stock, was treated according to the method of Fieser[65] to give the colorless liquid, b.p. 75-76°; reported[65] b.p. 78.8°.

2. 10-Undecenoyl Chloride

Thionyl chloride, 300 g. (2.52 moles), was allowed to react with 394 g. (2.14 moles) of 10-undecylenic acid, according to the procedure reported by Kapp and Knoll,[66] to yield 327 g. (76%) of 10-undecenoyl chloride, b.p. 78-80° (0.5 mm.); reported[66] b.p. 128° (13 mm.).

3. 9-Decenyl Isocyanate

This compound was prepared by following the procedure outlined by Allen and Bell[67] for synthesizing undecyl isocyanate. Into a 3-l., three-necked flask, equipped with a reflux condenser, mechanical stirrer, thermometer and addition funnel, were placed 147 g. (2.26 moles) of purified sodium azide (Fisher) and 500 ml. of

water. The reaction vessel was immersed in an ice-water bath, and a mixture of 327 g. (1.62 moles) of 10-undecenoyl chloride and 500 ml. of acetone was added at such a rate that the reaction temperature remained at 10-15°. The mixture was then cooled to 0° and stirred for 1 hour. The organic layer was removed and added slowly to 1.6 l. of prewarmed (60-70°) benzene in an open beaker, and the solution was held at this temperature, with occasional stirring, until effervescence had ceased. The benzene was removed by distillation at atmospheric pressure, and the residue was distilled through a 12-in., helix-packed column to yield 110 g. (38%) of 9-decenyl isocyanate, b.p. 92-94° (2 mm.), n_D^{20} 1.4485. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3010, 2940, 2900 (C-H); 2265 (NCO); 1640 (C=C); 1470, 1355 (CH_2 deformations); 997 (=CH-); 912 (CH_2=).

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.90; H, 10.56; N, 7.73. Found: C, 73.26; H, 10.30; N, 7.73.

4. β-Allyloxypropanoyl Chloride

The procedure for preparing 10-undecenoyl chloride was followed. Reaction of 235 g. (1.98 moles) of thionyl chloride with 194 g. (1.49 moles) of β-allyloxypropanoic acid produced 150 g. (68%) of β-allyloxypropanoyl chloride, b.p. 40-45° (1-2 mm.).

5. β-Allyloxyethyl Isocyanate

Using the same method as for the preparation of 9-decenyl isocyanate, 110 g. (0.74 mole) of β-allyloxypropanoyl chloride was caused to react with 74.4 g. (1.14 moles) of sodium azide to yield 55 g. (56%) of β-allyloxyethyl isocyanate, b.p. 59° (12 mm.), n_D^{20} 1.4320. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3120, 3000, 2930 (C-H); 2260 (NCO); 1650 (C=C); 1430, 1350 (CH_2 deformations); 1280, 1250, 1110 (ether); 995 (=CH-); 930, 868, 820 (CH deformations). This compound was a strong lachrymator.

Anal. Calcd. for $C_5H_9NO_2$: C, 56.70; H, 7.15; N, 11.01. Found: C, 56.93; H, 7.35; N, 11.22.

6. Acrylyl Chloride

According to the procedure of Stempel, Cross and Mariella,[68] 216 g. (3.0 moles) of acrylic acid was caused to react with 844 g. (6.0 moles) of benzoyl chloride (Matheson, Coleman and Bell) to yield 185 g. (68%) of acrylyl chloride, b.p. 74-75°; reported[69] b.p. 72-74°.

7. Vinyl Isocyanate

Into a 1-l., three-necked flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, mechanical stirrer, thermometer and addition funnel, were placed 106 g. (1.6 moles) of purified sodium azide

(Fisher), 300 ml. of water and 1.0 g. of hydroquinone. The reaction vessel was immersed in an ice-water bath, and a mixture of 100 g. (1.1 moles) of acrylyl chloride and 300 ml. of benzene was added at such a rate that the reaction temperature remained at 10-15°. The mixture was cooled to 0° and stirred for 6 hours. The organic layer was removed and dried over calcium chloride for 24 hours. The azide solution and 1.0 g. of hydroquinone were added to 1.0 l. of dry benzene in a 2-l., three-necked flask equipped with a magnetic stirring bar, thermometer and dry ice-acetone reflux condenser guarded by a calcium chloride drying tube. The reaction mixture was heated, with stirring, to 70-80° until the evolution of nitrogen was nil and then distilled through a 12-in. Vigereux column fitted with an ice-water condenser backed by a dry ice-acetone trap. The latter was guarded by a calcium chloride drying tube. Distillation was continued until a vapor temperature of 80° was reached. The distillates in the receiving flask and dry ice-acetone trap were combined and redistilled from 1.0 g. of hydroquinone through a 12-in., helix-packed column into a receiving flask that contained 200 ml. of dry benzene and 1.0 g. of hydroquinone. The receiving flask was immersed in a dry ice-acetone bath. The product was 40 g. (53%) of vinyl isocyanate, b.p. 39°, n_D^{20} 1.4180; reported[30] b.p. 39°, n_D^{20} 1.4188. Infrared

analysis revealed the following absorption bands ($cm.^{-1}$): 3100 (C-H); 2270 (NCO); 1630 (C=C); 1460, 1380, 1310 (CH deformations); 957 (=CH-); 895 (CH_2=); 835 (CH deformation). This compound was a severe lachrymator.

Anal. Calcd. for C_3H_3NO: C, 52.16; H, 4.38; N, 20.26. Found: C, 51.93; H, 4.31; N, 19.91.

C. Preparation of Derivatives

1. 9-Decenylurea

Into an open vial that contained 1.0 g. (0.055 mole) of 9-decenyl isocyanate and 3.0 ml. of dry benzene was bubbled gaseous ammonia until a piece of damp, red litmus paper, held above the solution, turned blue. An immediate exothermic reaction took place with the formation of a curdy, white precipitate. The latter was removed by filtration and recrystallized twice from 95% ethanol and once from water and dried under vacuum (25 mm.) at 50° to yield 0.88 g. (81%) of 9-decenylurea, m.p. 99-100°. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3250 (N-H); 2945 (C-H); 1660 ($-CONH_2$); 1605 (-CONH-); 1540 (NH deformation); 990 very weak (=CH-); 910 (CH_2=).

Anal. Calcd. for $C_{11}H_{22}N_2O$: C, 66.60; H, 11.25; N, 14.13. Found: C, 66.79; H, 11.08; N, 13.98.

2. N, N'-Di(9-decenylurea)

Into an open vial that contained 2.0 ml. of acetone were placed 1.0 g. (0.055 mole) of 9-decenyl isocyanate and 1 drop of distilled water. One drop of pyridine was added, and the solution was warmed gently on a hot plate until the volume was one-half that of the original. The resulting crystals were removed by filtration, washed with petroleum ether and 50% ethanol and recrystallized once from 95% ethanol. They were then dried under vacuum (25 mm.) at 50° to obtain 0.47 g. of white, slightly greasy crystals. The combined washings were concentrated on a hot plate and cooled in a dry-ice bath to obtain an additional 0.20 g. of product after washing, recrystallization and drying. The total yield was 0.67 g. (72%) of N,N'-di(9-decenylurea), m.p. 84-85°. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 2940, 2860 (C-H); 1630 (C=C); 1575 (-CONH-); 1475, 1250 (CH_2 deformations); 990 (=CH-); 910 (CH_2=).

Anal. Calcd. for $C_{21}H_{40}N_2O$: C, 74.92; H, 12.00; N, 8.32. Found: C, 74.70; H, 11.96; N, 8.42.

This same product was formed by allowing 9-decenyl isocyanate to remain in an open beaker overnight.

3. β-Allyloxyethylurea and N,N'-Di(β-allyloxyethylurea)

The method for preparing the corresponding 9-decenyl compounds was followed. The products obtained were viscous, yellow oils at room temperature.

4. N-(p-Tolyl), N'-(β-Allyloxyethylurea)

To 1.0 ml. of dry benzene in an open vial were added 0.20 g. (0.015 mole) of β-allyloxyethyl isocyanate, 0.20 g. (0.019 mole) of p-toluidine (Matheson, Coleman and Bell) and 1 drop of pyridine. The solvent was evaporated under vacuum, and the resulting crystals were washed with petroleum ether and 50% ethanol. The product was recrystallized once from 95% ethanol and once from water and dried under vacuum (25 mm.) at 50° to yield 0.23 g. (65%) of N-(p-tolyl), N'-(β-allyloxyethylurea), m.p. 82-83°. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3350 (N-H); 2950, 2890 (C-H); 1640 (C=C); 1575 (-CONH-); 1530 (NH deformation); 1450 (CH_3-); 1245, 1085 (ether); 1050 (aromatic); 997 (=CH-); 943 [?]; 812 (aromatic).

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.63; H, 7.76; N, 11.95. Found: C, 66.35; H, 7.58; N, 12.00.

5. Vinylurea

To 2.0 ml. of dry benzene in an open vial was added 0.50 g. (0.072 mole) of vinyl isocyanate. Immediately, gaseous ammonia was bubbled into the solution to yield a gelatinous, white precipitate which was separated by filtration and dried under vacuum (25 mm.) at 50°. The product was 0.50 g. (80%) of vinylurea, m.p. 68-70°;

reported[27] m.p. 80-81°*. Infrared analysis revealed the following absorption bands (cm.$^{-1}$): 3250 (N-H); 1665 (-CONH$_2$); 1600 (-CONH-); 1550 (NH deformation); 1410, 1325, 1225, 1135, 1075 (CH deformations); 980 (=CH-); 915 (CH$_2$=); 850, 840 (CH deformations).

Anal. Calcd. for $C_3H_6N_2O$: C, 41.86; H, 6.98; N, 32.56. Found: C, 41.56; H, 7.25; N, 32.34.

Two separate preparations of vinylurea gave products with the respective melting points of 72-73° and 73-74°. Attempts at recrystallizing the product from ethanol resulted in a loss of the material. Vinylurea crystals were converted to a viscous, yellow liquid while standing at room temperature in a screw-capped vial for several weeks.

6. N,N'-Divinylurea

Methods concerning the preparation of this compound are discussed later in this chapter.

D. Polymerizations

1. Source and Purification of Materials

Isocyanate monomers were stored in brown-glass sample bottles and were redistilled through a stainless-steel spinning-band column, having the equivalent of 23

*The melting point reported by Hart was determined by means of a Kofler hot-stage. Using this technique for the vinylurea prepared above also revealed a melting point of 80-81°.

theoretical plates, directly into glass tubes used for carrying out polymerizations. Other monomers were redistilled by conventional methods, with the exception of fumaronitrile which was recrystallized from water. These materials were then stored in brown-glass sample bottles in a vacuum desiccator.

The monomers used and their sources were as follows: styrene, maleic anhydride (Matheson, Coleman and Bell); methyl acrylate, methyl methacrylate, dimethyl maleate (Monomer-Polymer); fumaronitrile (Fisher). The initiators, dibenzoyl peroxide (Cadet) and α,α'-azodiisobutyronitrile (Eastman) were used as received.

Reagent grade benzene (Fisher) which had been stored over sodium ribbon was used as solvent for solution polymerizations.

2. Preparation of Polymers

Polymerization reactions were carried out in 40 X 15 mm. glass tubes which had constricted necks to allow sealing by means of a gas-air flame. The open end of a reaction tube was fitted with a rubber policeman and weighed to the nearest milligram. A predetermined amount of initiator, comonomer (where applicable) and solvent (where applicable) was added to the tube, and the tube and contents were weighed after each addition. The desired amount of isocyanate was distilled into the tube, the

policeman cap was replaced as rapidly as possible and the tube and contents were again weighed to the nearest milligram. The tube was cooled in a dry-ice bath in a nitrogen atmosphere. The policeman was removed, the tube was flushed with dry nitrogen by means of a glass capillary and was promptly sealed by heating the constricted neck with a gas-air flame.

Polymerizations were accomplished in the presence of ultraviolet light at room temperature or in an oven at 70-75° in the absence of light. No difference in the properties of products obtained by each of these methods was observed, and, unless noted otherwise, all polymers reported herein were prepared by ultraviolet initiation.

Both previously mentioned initiators were used. Again, no differences in product properties were noticed. Thus, all polymerizations reported are those which made use of dibenzoyl peroxide, unless a statement is made to the contrary.

After exposure, for a given period of time, to the conditions described above, a tube and its contents were cooled in a dry-ice bath, and the contents removed by breaking off the tube neck. Insoluble polymers were triturated with the nonsolvent by means of a mortar and pestle, and the solid was removed by filtration. If no liquid was present, the solid polymer was ground to a fine

powder. Rubbery polymers were broken into small pieces. Solutions of soluble polymers were poured with stirring into approximately 3 volumes of reagent grade petroleum ether (Fisher) to precipitate the polymer. The polymer was reprecipitated twice more by redissolving it in benzene and adding the resulting solution to petroleum ether, and the product was removed by filtration. All polymers were dried under vacuum (15 mm.) at 50-100°.

The details concerning copolymerizations of 9-decenyl isocyanate may be found in Table 2. Table 3 deals with copolymerizations of β-allyloxyethyl isocyanate, while the conditions for polymerizations and copolymerizations of vinyl isocyanate are recorded in Table 4. Other reactions that concern the polymerizations or attempted polymerizations of these monomers are described later in this chapter.

3. Characterization of Polymers

Polymer solubilities were determined by addition of 5-10 mg. of polymer to 0.5-1.0 ml. of solvent. If solution did not take place within a matter of minutes, the mixture was heated to the reflux temperature of the solvent and allowed to resume room temperature upon standing. Polymers were identified as soluble, partially soluble or insoluble. If no degree of solubility was observed in N,N-dimethylformamide, benzene, acetone, tetrahydrofuran, chloroform,

carbon tetrachloride, methylene chloride, ethyl acetate, dioxane, or dimethylsulfoxide, a polymer was classified as insoluble. Mixed solvent systems were not investigated. Once a polymer was found to be soluble in at least two separate solvents, no additional determinations were made. Normally, if a polymer was found to be insoluble in both benzene and N,N-dimethylformamide, no suitable solvent was discovered among the others mentioned. Insolubility of a polymer was assumed to be an indication that it was cross-linked.

Intrinsic viscosities of all materials were determined at 25° in either benzene or N,N-dimethyl-formamide. A discussion of the techniques and calculations involved may be found in any standard textbook of polymer chemistry.

Melt temperatures of polymers were determined by heating until they were liquified or decomposed or until a maximum of 300° was reached. Melting ranges reported are those at which a polymer softened until it was completely converted to a liquid which was generally colorless and, in some cases, quite viscous. Failure to melt at temperatures up to 300° was taken as further evidence that a polymer was cross-linked. Unless noted otherwise, all polymers reported were non-crystalline.

Infrared studies were made on the solid polymers in the form of potassium bromide discs. Isocyanate polymers, i.e., poly(vinyl isocyanate), exhibited strong absorptions characteristic of the -NCO group and showed no evidence of residual unsaturation upon examination of the region between 1000 cm.$^{-1}$ and 800 cm.$^{-1}$. Isocyanate copolymers exhibited varying degrees of isocyanate intensities which were consistent with their nitrogen content as determined by elemental analysis. In addition, the spectra of copolymers showed absorption bands characteristic of the comonomer used in their preparation. For instance, copolymers of methyl acrylate, methyl methacrylate and dimethyl maleate gave strong ester absorptions, while the spectra of styrene copolymers contained absorption bands found in polystyrene.

Elemental analysis provided a method for determining the ratio of the number of comonomer units to isocyanate units within a copolymer, according to the following equation:

$$\frac{14.01}{(\text{mol. wt. of isocyanate monomer}) + \frac{m_2}{m_1}(\text{mol. wt. of comonomer})} = \frac{\%N}{100}$$

where: $\frac{m_2}{m_1}$ = moles of comonomer per mole of isocyanate within the copolymer.

The results of the characterization of copolymers of 9-decenyl isocyanate, copolymers of β-allyloxyethyl isocyanate and polymers and copolymers of vinyl isocyanate are given in Tables 5, 6 and 7, respectively.

E. Other Polymerization Studies

1. Attempted Polymerization of 9-Decenyl Isocyanate and β-Allyloxyethyl Isocyanate

A sample of 1.0 ml. of 9-decenyl isocyanate plus 0.005 g. of dibenzoyl peroxide and a similar sample of β-allyloxyethyl isocyanate were prepared for polymerization according to the method described previously. Each sample was exposed to ultraviolet light for 1 week and placed in an oven at 70-75° for 1 week. The resulting solutions were poured into 3 volumes of petroleum ether. The latter was removed by evaporation, and the benzene solution was added to 3 volumes of p-dioxane. The solvents were removed by evaporation, and the residues were added to 3 volumes of methanol and concentrated under vacuum (15 mm.) at 50°. No cloudiness was observed during the attempted precipitations, and no solid remained as residue upon evaporation of solutions of either compound.

Similar attempts at solution polymerization of these compounds using α, α'-azodiisobutyronitrile produced the same results.

2. Copolymerization of 9-Decenyl Isocyanate and β-Allyloxyethyl Isocyanate with Maleic Anhydride

Two polymerization samples of each isocyanate were prepared by the same method. Each sample consisted of 0.5 g. of isocyanate, 0.5 g. of maleic anhydride and 0.005 g. of dibenzoyl peroxide. One sample of each isocyanate was exposed to ultraviolet light, and the others were placed in an oven at 70-75°. The samples in the oven were converted to a black tar within 1 hour, and discoloration was evident in the ultraviolet mixtures. At the end of 24 hours, all samples were hard, black, insoluble castings.

3. Polymerization of β-Allyloxyethyl Isocyanate

A sample of 0.72 g. of β-allyloxyethyl isocyanate was prepared for polymerization by the usual method. No initiator or solvent was added. The sample was placed in an oven at 70-75° for 2 weeks. The polymerization tube was opened, and the precipitate which had formed was removed by filtration, washed with acetone and dried under vacuum (15 mm.) at 50°. The product was 0.14 g. of a soluble, white powder, m.p. 135-145°. Its intrinsic viscosity was 0.037. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 2900 (C-H); 1715 wide (C=O); 1650 shoulder (C=C); 1460, 1350 (CH_2 deformations); 1275 (ether); 1180 [?]; 1110 (ether); 995 (-CH=); 927, 765 (CH deformations).

Anal. Calcd. for $(C_5H_9NO_2)_n$: C, 56.70; H, 7.15; N, 11.01. Found: C, 56.41; H, 6.96; N, 10.88.

4. Polymerization of Vinyl Isocyanate

A sample of 0.94 g. of vinyl isocyanate, free of initiator and solvent, was prepared for polymerization by the usual method and stored in the dark at room temperature for 1 month. The polymerization tube was opened, and the hard, white casting was removed, ground to a powder and dried under vacuum (15 mm.) at 50°. The product was 0.88 g. of a white, insoluble powder which did not melt at 300°. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 2940 weak (C-H); 2265 (NCO); 1700 weak (C=O); 1630 weak (C=C); 1430, 1115 (CH_2 and CH deformations).

Anal. Calcd. for $(C_3H_3NO)_n$: C, 52.16; H, 4.38; N, 20.26. Found: C, 51.96; H, 4.21; N, 19.90.

5. Copolymerization of Vinyl Isocyanate with Maleic Anhydride

A polymerization sample consisting of equal weights of vinyl isocyanate and maleic anhydride and 0.5% dibenzoyl peroxide was prepared as usual. An immediate reaction caused the solid maleic anhydride to turn from white to brown. After exposure to ultraviolet light, the brown solid was removed. It was insoluble and did not melt at 300°. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 2960 (C-H); 2265 (NCO); 1785, 1700 (C=O); 1560 [?]; 1250 wide (CH deformation).

F. Reactions of Copolymers

1. Source and Purification of Materials

Absolute ethanol was acquired from stock and used as received. All other reacting materials were redistilled by conventional methods before using. These materials and their sources were as follows: n-butylamine, 1,6-hexanediamine (Matheson, Coleman and Bell); 1,5-hexanediol (Eastman); ethylene glycol, ethylenediamine, water (stock).

2. Reaction Technique

Ethanol and n-butylamine were used in their pure forms. Difunctional compounds, used as cross-linking agents, were added to reactions in the form of dilute dioxane solutions having a concentration of 2.0 mg. of cross-linking reagent per milliliter of reagent grade p-dioxane (Eastman). Reactions were carried out in screw-capped vials and in polymerization tubes as in the preparation of polymers. The same results were obtained in both types of reaction vessels, and no distinction shall be made as to which type was used for each reaction.

A sample of 25 mg. of copolymer was dissolved in 0.5-1.0 ml. of reagent grade p-dioxane (Eastman), and either 0.1 ml. of ethanol or n-butylamine or a calculated equivalent amount of cross-linking reagent was added. The reaction vessel was flushed with dry nitrogen, and 1 drop

of a 5% solution of triethylamine in p-dioxane was added. The vial or tube was immediately capped or sealed and placed in an oven at 70-90° for 24 hours. Vials and tubes were brought to room temperature, and their contents, including any insoluble material, were added to 3 volumes of water. The resulting solids were removed by filtration and dried under vacuum (15 mm.) at 50°. Yields were near quantitative in all cases.

The equivalent amount of a difunctional, active hydrogen-containing compound necessary to cross-link 25 mg. of copolymer can be calculated from the number of milli-equivalents of isocyanate per gram of copolymer which, in turn, is based on the nitrogen content of the copolymer:

$$\text{milliequivalents of NCO per g. of copolymer} = \frac{(\%N) \times (10)}{14.01}$$

$$\text{mg. of cross-linking agent per 25 mg. of copolymer} = \frac{\left(\text{milliequivalents of NCO per g. of copolymer}\right) \times \left(\text{equivalent weight of cross-linking agent}\right)}{40}.$$

3. Characterization of Products

The products of reactions between copolymers that contained reactive isocyanate groups and mono- and difunctional active hydrogen-containing compounds were characterized according to solubility, melt temperature, intrinsic viscosity and infrared absorption in the same manner as were the previously discussed polymers and

copolymers. All products of reactions of linear copolymers with n-butylamine or ethanol were readily soluble. Other properties of these products are given in Table 8 and Table 9, respectively. Properties of materials resulting from reactions of linear copolymers with difunctional reagents may be found in Tables 10 through 14.

G. Preparation and Polymerization of "N,N'-Divinylurea"

1. General Comments

Several attempts have been made to prepare pure, monomeric N,N'-divinylurea by means of the reaction of water with vinyl isocyanate. Both in the presence and absence of solvent (e.g., N,N-dimethylformamide, acetone) the reaction was immediately exothermic and effervescent, and the products were white solids which were at least partially polymeric. The degree of crystallinity of the products, which was always low, varied, as did their melting points, with each preparation. Reactions in solution generally gave soluble products having infrared spectra that revealed large amounts of unsaturation. Reactions in bulk yielded mostly unsaturated materials which were insoluble and did not melt at 300°.

Upon recrystallization by dissolving the white powder in ethanol and pouring the resulting solution into ether, a copious, white precipitate was formed which could

be removed by filtration or centrifugation. When exposed to the atmosphere, this precipitate immediately decomposed and was partially converted into a yellow, gummy polymer which became a white powder upon drying. The solubility of this decomposition product varied, as did its melting point, with each preparation.

When the product of the vinyl isocyanate-water reaction was placed in ethanol for 2 weeks in a closed container at approximately 20°, and an alcoholic solution of 2,4-dinitrophenylhydrazine reagent was added, a yellow precipitate was produced which, after recrystallization from ethanol, formed a highly crystalline, yellow solid. This material melted sharply on a Kofler micro hot-stage at 168°. Another crystalline material, which melted completely at 135°, was also isolated from the same ethanol solution.

2. Preparation I

In an open vial, immersed in dry ice, that contained 2.0 ml. of acetone, was placed 1.0 ml. of vinyl isocyanate and 2 drops of distilled water. The mixture was stirred occasionally and, after 1 hour, was filtered to remove a small amount of solid which had precipitated. The resulting solution was evaporated to dryness under vacuum at room temperature to yield a cream-colored, slightly gummy solid which exhibited a flow temperature of 45-50°. The product

was soluble in ethanol and N,N-dimethylformamide. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3000 (C-H); 1660 (C=O); 1635 (C=C); 1550 (NH deformation); 1390, 1260 (CH deformations); 1145, 1080, 1070 [?]; 985 (-CH=); 935, 875, 855 (CH deformations).

3. Preparation II

To a 50-ml., three-necked flask, equipped with a mechanical stirrer, reflux condenser with a nitrogen inlet, and a hypodermic syringe in a rubber plug, were added 15 ml. of acetone and 3.98 g. (0.058 mole) of vinyl isocyanate. By means of the hypodermic syringe, 0.569 ml. (0.029 mole) of distilled water was added over a period of 45 minutes. The mixture was stirred an additional 2 hours under a positive nitrogen pressure and was kept below the reflux temperature of the isocyanate by cooling in a dry-ice bath. The resulting precipitate, after being removed by filtration and dried under vacuum (25 mm.) at 50°, was 1.66 g. of a partially crystalline, white solid, m.p. 180° (with decomposition).* The product was soluble in ethanol and N,N-dimethylformamide and possessed an intrinsic viscosity of 0.036. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3000 (C-H); 1700 - 1500 wide (C=O, -CONH-

*On a Kofler micro hot-stage, this same material melted with decomposition at 200-205°.

and NH deformation); 1450, 1370, 1245 (CH_2 and CH deformations); 982 (=CH-); 845 (CH deformation).

Anal. Calcd. for $C_5H_8N_2O$: C, 53.54; H, 7.20; N, 24.98. Found: C, 52.58; H, 6.96; N, 24.67.

The resulting acetone solution was used for polymerization studies.

4. Polymerization I

Approximately 0.5 g. of the product from preparation I (above) was dissolved in 10 ml. of absolute ethanol. A 2.0 ml. portion of this solution and 0.005 g. of dibenzoyl peroxide were prepared for polymerization in a sealed tube and placed in an oven at 70° for 1 week. The resulting clear, yellow solution was evaporated to dryness under vacuum at room temperature. The yellow, gummy residue was washed with petroleum ether and dried to yield a soluble yellow powder, m.p. 180-185° (with decomposition). The intrinsic viscosity of this material was 0.042. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3000 (C-H); 1650 (-CONH-); 1540 (NH deformation); 1445, 1375, 1315, 1245, 715 (CH_2 and CH deformations).

Anal. Calcd. for $(C_5H_8N_2O)_n$: N, 24.98. Found: N, 21.70.

5. Polymerization II

A sample (0.075 g.) of the product from preparation

II (above) and 0.001 g. of α, α'-azodiisobutyronitrile was dissolved in 2.0 ml. of ethanol and prepared for polymerization in a sealed tube. The sample was exposed to ultraviolet light for 7 hours. The resulting precipitate was removed by filtration and dried under vacuum (15 mm.) at 50° to yield 0.046 g. of white powder. This material was insoluble and did not melt at 300°. The filtrate was concentrated under vacuum and added to 3 volumes of petroleum ether to produce a white precipitate which was dried under vacuum (15 mm.) at 50°. The product was 0.010 g. of yellow powder, m.p. 175-200° (with decomposition), which was soluble in N,N-dimethylformamide. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3000 (C-H); 1640 wide (-CONH-); 1540 wide (NH deformation); 1440, 1375, 1240, 1110 wide, 850 wide (CH_2 and CH deformations).

Anal. Calcd. for $(C_5H_8N_2O)_n$: N, 24.98. Found: N, 21.90.

5. Copolymerization I

A sample of 3.0 ml. of the acetone solution remaining from preparation II (above), 0.53 g. of styrene and 0.01 g. of α, α'-azodiisobutyronitrile was prepared for polymerization by the usual method and exposed to ultraviolet light for 29 hours. The resulting mixture was filtered to yield 0.10 g. of insoluble, white powder which did not melt at 300°. The filtrate was added to petroleum ether to cause

precipitation of 0.10 g. of a soluble, cream-white solid, m.p. 227-230°. The petroleum ether solution was concentrated and added to methyl alcohol to give a white precipitate. This was removed by filtration and dried under vacuum (15 mm.) at 50°. The product was 0.068 g. of a soluble, non-crystalline, white powder, m.p. 83-95°, which possessed an intrinsic viscosity of 0.131. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 3025, 2940 (C-H); 1625 (-CONH-); 1600, 1480 (aromatic); 1445, 1355, 1025 (CH_2 and CH deformations); 757, 698 (aromatic).

Anal. Found: N, 2.55.

6. Copolymerization II

A 1.0 ml. portion of freshly distilled vinyl isocyanate was placed in a vial with 2.0 ml. of acetone, and 2 drops of water were added. The solution was stirred vigorously for a few minutes and sealed in a polymerization tube with 0.5 ml. of styrene and 0.01 g. of α, α'-azodiisobutyronitrile. After exposure to ultraviolet light for 3 days, the clear, yellow solution was added to petroleum ether, and the resulting precipitate was removed by filtration and dried under vacuum (15 mm.) at 50°. The product was 0.10 g. of a soluble, cream-yellow solid, m.p. 135-160°. The intrinsic viscosity of this material was

0.060. Infrared analysis revealed the following absorption bands ($cm.^{-1}$): 2940 (C-H); 1640 wide (-CONH-); 1545 (NH deformation); 1440, 1320, 1220, 1135, 1025 (CH_2 and CH deformations); 980, 847, 755 wide (aromatic).

Anal. Found: N, 15.34.

7. Hydrogenation

The product of preparation II (above) was hydrogenated, using a platinum oxide catalyst, at 20° and atmospheric pressure according to the method of Stone.[53] A sample of 0.10 g. absorbed 17.5 ml. of hydrogen gas. This represents 41% of the theoretical value calculated for N,N'-divinylurea. Both styrene copolymers were treated according to the same method, but failed to absorb any hydrogen.

TABLE 2

COPOLYMERIZATIONS OF 9-DECENYL ISOCYANATE

Polymer No.	Comonomer	Weight of Comonomer g.	Weight of Isocyanate g.	M_2/M_1[a]	Initiator %	Solvent ml.	Reaction Time
1	methyl acrylate	0.51	0.51	2.1	0.5	---	1.0 wk.
2	methyl acrylate	0.86	0.97	1.9	0.6	2.0	1.0 hr.
3	styrene	0.44	0.54	1.4	0.5	---	1.0 wk.
4	styrene	0.50	1.01	0.9	0.7	1.0	3.8 da.
5	methyl methacrylate	0.50	1.06	0.9	0.7	1.0	1.6 da.
6	dimethyl maleate	0.70	0.88	1.0	0.7	1.0	1.0 wk.

[a] $\frac{M_2}{M_1} = \frac{\text{moles of comonomer}}{\text{moles of isocyanate}}$ in feed.

TABLE 3

COPOLYMERIZATIONS OF β-ALLYLOXYETHYL ISOCYANATE

Polymer No.	Comonomer	Weight of Comonomer g.	Weight of Isocyanate g.	$\frac{M_2}{M_1}$ [a]	Initiator %	Solvent ml.	Reaction Time
7	methyl acrylate	0.51	0.51	1.5	0.5	---	1.0 wk.
8	methyl acrylate	0.49	0.32	2.3	1.2	1.0	1.2 hr.
9	styrene	0.45	0.56	1.0	0.5	---	1.0 wk.
10	styrene	0.54	0.36	1.8	1.1	1.0	2.5 da.
11	methyl methacrylate	0.45	0.37	1.5	1.2	1.0	1.9 da.
12	dimethyl maleate	0.34	0.56	0.5	1.1	1.0	1.0 wk.

[a] Previously defined.

TABLE 4

POLYMERIZATIONS AND COPOLYMERIZATIONS OF VINYL ISOCYANATE

Polymer No.	Comonomer	Weight of Comonomer g.	Weight of Isocyanate g.	$\frac{M_2}{M_1}$[a]	Initiator %	Solvent ml.	Reaction Time
13	---	---	0.90	---	0.5	---	2.0 da.
14	---	---	0.29	---	3.2	2.0	3.0 hr.
15	methyl acrylate	0.59	0.51	0.9	0.5	---	1.0 wk.
16	methyl acrylate	0.91	0.22	3.3	0.9	1.0	0.5 hr.
17	styrene	0.47	0.62	0.5	0.5	---	1.0 wk.
18	styrene	0.90	0.22	2.7	0.9	1.0	1.2 da.
19	methyl methacrylate	0.50	0.31	1.1	0.5	1.0	5.0 hr.
20	fumaronitrile	0.78	0.32	2.1	0.9	5.0	1.5 hr.

[a]Previously defined.

TABLE 5

COPOLYMERS OF 9-DECENYL ISOCYANATE

Polymer No.	Yield g.	Recovery %	Description of Product	Melting Range °C.	Intrinsic Viscosity	Elemental Analysis %N	$\frac{m_2}{m_1}$ [a]
1	0.93	93	insoluble, rubbery solid	>300	---	2.62	4
2	0.25	14	soluble, rubbery solid	80-100	0.78	0.60	25
3	0.31	32	soluble, colorless solid	125-145	0.40	0.56	22
4	0.18	12	soluble, colorless solid	140-150	0.39	0.62	20
5	0.47	30	soluble, colorless solid	140-150	0.16	0.95	13
6	0.27	17	insoluble, gummy solid	>300	---	4.07	1

[a] $\frac{m_2}{m_1} = \frac{\text{moles of comonomer}}{\text{moles of isocyanate}}$ in copolymer.

TABLE 6

COPOLYMERS OF β-ALLYLOXYETHYL ISOCYANATE

Polymer No.	Yield g.	Recovery %	Description of Product	Melting Range °C.	Intrinsic Viscosity	Elemental Analysis %N	$\frac{m_2}{m_1}$ [a]
7	0.90	90	insoluble, rubbery solid	>300	---	1.83	7
8	0.25	31	soluble, colorless solid	80-100	0.55	0.20	80
9	0.15	15	soluble, colorless solid	120-150	0.35	0.25	53
10	0.24	27	soluble, colorless solid	115-135	0.10	0.11	120
11	0.38	46	soluble, colorless solid	116-124	0.13	1.15	11
12	0.12	13	insoluble, rubbery solid	>300	---	3.11	2

[a] Previously defined.

TABLE 7

POLYMERS AND COPOLYMERS OF VINYL ISOCYANATE

Polymer No.	Yield g.	Recovery %	Description of Product	Melting Range °C.	Intrinsic Viscosity	Elemental Analysis %N	$\frac{m_2}{m_1}$ [a]
13	0.90	100	insoluble, hard, white solid	>300	---	19.96	---
14	0.18	62	insoluble, soft, white solid	>300	---	---	---
15	0.67	61	insoluble, rubbery solid	>300	---	10.13	1
16	0.22	19	insoluble, rubbery gel	>300	---	6.03	2
17	0.90	83	insoluble, white solid	>300	---	4.70	2
18	0.20	18	soluble, colorless solid	110-125	0.44	1.26	10
19	0.12	15	soluble, colorless solid	115-128	0.22	1.42	9
20	0.28	25	insoluble, yellow-white solid	>300	---	---	---

[a] Previously defined.

TABLE 8

REACTIONS WITH n-BUTYLAMINE

Polymer No.	Description of Product	Melting Range °C.	Intrinsic Viscosity
2	yellow, rubbery solid	----	0.76
3	white, chalky solid	142-155	0.33
5	white, powdery solid	162-178	0.16
8	yellow-white, rubbery solid	100-120	0.31
10	white, powdery solid	120-140	0.16
11	white, powdery solid	153-163	0.11
18	white, chalky solid	130-140	0.38

TABLE 9

REACTIONS WITH ETHANOL

Polymer No.	Description of Product	Melting Range °C.	Intrinsic Viscosity
2	white, rubbery solid	125-160	0.61
3	white, chalky solid	130-140	0.36
4	white, chalky solid	130-140	0.36
5	white, powdery solid	110-135	0.18
8	white, rubbery solid	----	0.53
9	white, chalky solid	130-140	0.28
11	white, powdery solid	150-160	0.20
19	white, powdery solid	120-130	0.24

TABLE 10

REACTIONS WITH ETHYLENEDIAMINE

Polymer No.	Description of Product	Melting Range °C.	Solubility
2	yellow, brittle solid	>300	insoluble
5	yellow-white solid	>300	slowly soluble
8	yellow solid	>300	insoluble
11	white solid	>300	partially soluble
18	white solid	>300[a]	partially soluble

[a]Partially melted at 135-145°.

TABLE 11

REACTIONS WITH ETHYLENE GLYCOL

Polymer No.	Description of Product	Melting Range °C.	Solubility
2	yellow-white solid	>300	insoluble
5	white solid	>300[a]	soluble
11	white solid	>300	slowly soluble

[a]Partially melted at 160-190°.

TABLE 12

REACTIONS WITH 1,6-HEXANEDIAMINE

Polymer No.	Description of Product	Melting Range °C.	Solubility
5	white solid	167-175	partially soluble
8	cream-yellow, rubbery solid	>300	insoluble

TABLE 13

REACTIONS WITH 1,5-HEXANEDIOL

Polymer No.	Description of Product	Melting Range °C.	Solubility
2	yellow-white solid	>300	insoluble
3	white, flaky solid	>300[a]	partially soluble
5	white solid	>300	soluble
8	orange, rubbery solid	>300	insoluble
11	white, powdery solid	>300[b]	slowly soluble

[a]Partially melted at 125-135°.

[b]Partially melted at 170°.

TABLE 14

REACTIONS WITH WATER

Polymer No.	Description of Product	Melting Range °C.	Solubility
2	brittle solid	>300	insoluble
4	white, chalky solid	150-200	soluble
5	white solid	>300	insoluble
11	white solid	>300	soluble

CHAPTER V

RESULTS AND CONCLUSIONS

A. Synthesis of Monomers

The Curtius rearrangement was found to be a suitable means for the preparation of unsaturated isocyanates. No difficulty was encountered in preparing the corresponding acyl chlorides, azides and isocyanates from 10-undeceylenic acid and β-allyloxypropanoic acid even though yields of the final products were lower than those reported for saturated isocyanate preparations. The low yields may have been due to the use of unactivated, commercial-grade sodium azide. It has been reported[33] that individual lots of this material vary greatly in their reactivity and that the reactivity of a given lot varies with age. Activation of the commercial product according to the procedure of Nelles[69] has been found to increase the reactivity of sodium azide.[33]

The low yield of vinyl isocyanate is further explained in that the high reactivity of the olefinic and -NCO groups caused considerable formation of polymeric by-product within the reaction vessel. Hydroquinone may

not have been a suitable inhibitor of the undesirable side reaction, since it is theoretically capable of undergoing a reaction with the isocyanate. It is believed that an inhibitor which does not contain active hydrogen, e.g., quinone, would have been more appropriate. Rearrangement of the acrylyl azide in nitrobenzene might be a possibility for future preparations. Dinitrobenzenes are capable of retarding free radical reactions.[70] Such a solvent would also enable rearrangement of the acrylyl azide at a higher temperature. This might be desirable since, in this work, it was noticed that nitrogen evolution, from the reacting azide solution, was not predominant until the boiling point of the benzene solvent had been reached. Hart[71] reports the use of toluene, in which the acrylyl azide was decomposed at 80-85°.

Storage in a vacuum desiccator, which had been flushed with nitrogen, was satisfactory for 9-decenyl and β-allyloxyethyl isocyanates. Additional precautions were necessary in the case of the more reactive vinyl isocyanate. In order to reduce the formation of insoluble polymer, it was necessary to store this monomer in the form of a benzene solution. Again, nitrobenzene might have been more efficient in this respect. A small amount of dinitrobenzene, added to the benzene solution, might also be capable of retarding polymer formation.

Because of the high volatility and lachrymatory properties of vinyl and β-allyloxyethyl isocyanates, it was necessary to open the respective storage containers in a hood, thus exposing these compounds to atmospheric humidity. Some degree of contamination may have resulted during such an operation.

B. Preparation of Derivatives

The reactivity of isocyanates with active hydrogen attached to a nitrogen atom was exhibited as both 9-decenyl and vinyl isocyanate reacted spontaneously with ammonia. Such a degree of reactivity was not as obvious in the case of β-allyloxyethyl isocyanate. The stability of the derivatives of 9-decenyl and β-allyloxyethyl isocyanates was not questionable, but a certain degree of instability of vinyl ureas was obvious. This was attributed to isomerism.

It is known that such N-ethylene compounds, by means of the hydrogen atom on the nitrogen, tautomerize into imine derivatives. This behavior is not unlike the keto-enol tautomerism which takes place during the isomerism of vinyl alcohol into acetaldehyde. Thus, upon heating vinylurea in aqueous solution in the presence of a trace of phosphoric acid, it decomposes into acetaldehyde and

urea.[27] This phenomenon has been explained according to the following reactions:

$$H_2C{=}CH{-}NHCONH_2 \rightleftharpoons H_3C{-}CH{=}NCONH_2 \qquad (13)$$

$$H_3C{-}CH{=}NCONH_2 \xrightarrow{H_2O} H_3C{-}CHO + H_2NCONH_2 \qquad (14)$$

The action of atmospheric humidity has been found to be sufficient to decompose isopropenylurea into acetone and urea.[27]

The instability of 1-alkenyl ureas is evident during the determination of melting points. Hart[27] has reported several cases in which a notable difference was observed between melting points obtained in capillary tubes and those established by the Kofler method. As great a difference as 27° was noted in one case. Sato[30] showed that the melting points of some N-1-alkenyl, N'-alkyl (or aryl) ureas varied with the speed of heating, as well as with the techniques of preparation.

The results described in the previous chapter would certainly seem to support those obtained by Hart and Sato.

Infrared studies have been made to determine the contribution of each of the isomeric structures in α,β-unsaturated ureas. Sato[30] found that nonsubstituted vinyl ureas isomerized to a mixture of the C=C and C=N double-bond-containing compounds, whereas N-1-substituted vinyl

ureas were present in nearly a pure state of the C=N isomer after heating at 40-50° or standing for a long period of time. Similar studies made in this laboratory gave no positive evidence of C=N absorption in vinylurea and N,N'-divinylurea due to the usually wide absorptions by C=C and C=O double bonds in the regions where C=N is active, i.e., 1650-1500 $cm.^{-1}$. Infrared studies in the region of 3000 $cm.^{-1}$ were restricted because of the presence of atmospheric moisture and the consequent OH absorption band. Relative humidity readings were always greater than 50%.

C. Polymerizations

Neither 9-decenyl nor β-allyloxyethyl isocyanate could be homopolymerized by free radical initiation.

Vinyl isocyanate was polymerized in bulk and in solution to yield insoluble, infusible products. The fact that a soluble, linear polymer could not be obtained from this monomer should not be too surprising, however. It is well known that, at temperatures above 0°, isocyanic acid polymerizes readily to the cyclic trimer, isocyanuric acid.[72] There have also been reports of isocyanates that polymerize readily to isocyanurates[33] and others that polymerize on heating.[3] Such reactions have already been discussed. Hart[71] found that vinyl and isopropenyl

isocyanates polymerized to insoluble solids while standing at room temperatures and that copolymers with other vinyl monomers could be formed in the same manner.

Infrared spectra of the insoluble vinyl isocyanate polymers generally exhibited no evidence of unsaturation in the region of 1000-800 $cm.^{-1}$, thus indicating polymerization through the vinyl group. While these same spectra showed strong absorptions characteristic of -NCO, there were also bands in the region between 1800 $cm.^{-1}$ and 1700 $cm.^{-1}$ which are believed to be those characteristic of dimer and trimer formation. Therefore, it is suggested that the poly(vinyl isocyanates) resulted from reactions through both the isocyanate groups and the carbon-carbon double bonds.

The spectra of poly(vinyl isocyanate) also contained weak to strong absorption bands in the region 1655-1640 $cm.^{-1}$. While these may be due to residual unsaturation, they could also be caused by amide linkages, and it is impossible at this time to exclude the possibility of cross-linking due to an impurity (i.e., moisture).

D. Copolymerizations

Copolymers of the unsaturated isocyanates studied herein, which contained a relatively high percentage of

nitrogen and generally had a comonomer to isocyanate ratio of 7:1 or less, were found to be cross-linked as evidenced by their insolubility and thermal resistance. In preparing these, as well as the polymers of vinyl isocyanate, greatest care was taken to exclude water from the time of final distillation of the isocyanate until the resulting polymer was purified. This included handling of the materials in a nitrogen atmosphere, transporting them in vacuum desiccators, thorough drying of apparatus and storing of polymers in vacuum desiccators until characterization was completed.

Infrared spectra of insoluble, infusible copolymers did show absorption in the region of 1650-1630 $cm.^{-1}$ which could possibly be assigned to carbonyl bands characteristic of substituted ureas. However, other characteristic absorptions of the suspected amide linkage were generally absent, with the exception of a few cases involving vinyl isocyanate. For example, there were no amide II bands which should be found between 1615 $cm.^{-1}$ and 1555 $cm.^{-1}$ according to Moelants and Hart[52] or in the region of 1630-1580 $cm.^{-1}$ according to Boivin and his coworker.[51] Therefore, it is reasoned that premature cross-linking was not a result of reaction of the monomers or polymers with water during the polymerization operations. Rather, it is postulated that said cross-linking was related in some way to the reactions of isocyanates to form dimers and trimers.

Infrared spectra of the insoluble products generally showed absorption bands between 1800 $cm.^{-1}$ and 1700 $cm.^{-1}$ which have been assigned to carbonyl absorptions like those found in isocyanate dimers and trimers. Further, such polymers, i.e., poly(vinyl isocyanate), were found to have the same elemental composition as the monomer. If a substituted urea had been formed, the carbon, hydrogen and nitrogen content should have been higher than that of the monomer and not slightly lower, as was the actual case. Still further, β-allyloxyethyl isocyanate, which would not homopolymerize or react with water to give a solid derivative, when placed under simulated polymerization conditions, produced a soluble, low-melting, white solid which exhibited no NCO absorption in the infrared. However, unsaturation was noted as well as a strong absorption at 1715 $cm.^{-1}$. The band at 1715 $cm.^{-1}$ is characteristic of isocyanate trimers. This compound also gave the same elemental analysis as did the monomeric isocyanate.

Although 9-decenyl and β-allyloxyethyl isocyanates would not polymerize under free radical conditions, they copolymerized with dimethyl maleate to give products with relatively high nitrogen content. Dimethyl maleate itself is practically unreactive as a monomer, but is capable of copolymerizing under free radical conditions.

Attempted copolymerization of isocyanate monomers with maleic anhydride gave only insoluble decomposition products. Such results seem consistent with the fact that anhydrides are capable of reacting with isocyanates.

In general, there was a greater certainty of solution polymerizations resulting in the formation of soluble products than when bulk polymerization techniques were employed. Perhaps there would be even more certainty of obtaining soluble polymers and copolymers if more highly dilute solutions of unsaturated isocyanates were used for such reactions.

An additional suggestion, which might pertain to this and similar studies, concerns the use of thermally unstable isocyanate generators. A number of isocyanate reactions are known to be reversible. Products of reactions of isocyanates with amines, alcohols, phenol and sodium bisulfite can be heated to regenerate the reactants.[4] Isocyanate adducts of this type have previously been used in applications where it was necessary to delay the desired isocyanate-substrate reaction until the final stages of fabrication. The temperature at which a substituted isocyanate will dissociate depends on the nature of the isocyanate as well as that of the substituent.

Applying the above technique to the problem at hand, an unsaturated isocyanate derivative, e.g., the sodium

bisulfite adduct of vinyl isocyanate, might be polymerized to yield a linear polymer which contained the corresponding "masked" isocyanate groups. This polymer could then be placed in the presence of a desirable reactant, e.g., n-butylamine or ethylenediamine, and the mixture heated to the necessary temperature to cause dissociation of the isocyanate adducts, thus enabling the free isocyanate groups to react to form, respectively, a linear or cross-linked polyurea. It should be pointed out that possible side reactions during dissociation could limit the use of such materials to some extent.

In the present study, only copolymerization reactions were successful in producing linear, high-molecular-weight products that contained reactive isocyanate groups. The relative amounts of isocyanate in all products were calculated from the results of elemental analysis. It was necessary to use this method since the materials which were insoluble did not lend themselves to the conventional volumetric or gravimetric techniques of quantitative analysis.

E. Reactions of Copolymers

Soluble copolymers that contained reactive isocyanate groups were caused to react with both n-butylamine and ethanol to yield soluble products which exhibited

properties different than those of the starting materials. Whereas the original copolymers were generally clear and colorless, the products were white powders. Although no general trend was noticed, the new copolymers had melt temperatures different from the parent polymeric compounds. Normally, the intrinsic viscosities of the substituted urea and urethane copolymers were less than those of the corresponding polyisocyanates. Methyl methacrylate copolymers were an exception however.

Infrared spectra of the above products showed complete absence of NCO absorption in addition to new absorptions in the regions 1640-1600 cm.$^{-1}$ and 1600-1550 cm.$^{-1}$. The former were attributed to the amide band I and the latter to the amide band II and NH deformation. Otherwise, infrared spectra of the products were the same as those of the reactants.

It has further been shown that highly soluble polyisocyanates may be converted to slowly or partially soluble to insoluble materials by reaction with difunctional active hydrogen-containing compounds. These products exhibited higher melting points than the linear polymers and, in general, did not melt at temperatures up to 300°.

The cross-linked polyureas and polyurethanes were generally white to yellow solids. Some were rubbery, but these resulted from gummy starting materials. In several

cases, the product had completely absorbed the solvent in which the cross-linking reaction had taken place. Infrared spectra of these materials, while showing no isocyanate absorption, revealed new bands that could be assigned to amide band I, amide band II and NH deformation.

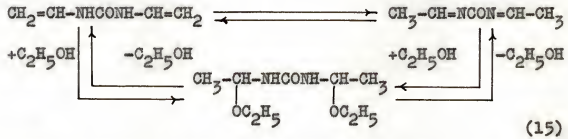
It should be mentioned at this point that in several cases, when using isocyanate copolymers which had low intrinsic viscosities as well as low nitrogen content, cross-linking was not evident. Infrared spectra of the products were the same as for cross-linked materials, but melting points were well below 200° and the materials were highly soluble. These results seem consistent with the knowledge that cross-linked structures are possible only in systems possessing structural units which are capable of joining with more than two other units.[56]

F. Preparation and Polymerization of "N,N'-Divinylurea"

Initial attempts to prepare N,N'-divinylurea resulted in the formation of partially soluble materials which were only slightly crystalline. Although infrared spectra of these products were quite similar to those of urea and substituted ureas, several showed new bands which could be attributed to carbonyl absorptions not associated with the amide group. The range of these absorptions was from 1750 $cm.^{-1}$ to 1650 $cm.^{-1}$. Infrared spectra also

showed varying amounts of unsaturation as evidenced by absorptions between 1000 cm.$^{-1}$ and 800 cm.$^{-1}$. Elemental analysis of these initial products gave values for carbon, hydrogen and nitrogen that were intermediate between the calculated values for N,N'-divinylurea and vinyl isocyanate. Therefore, it was assumed that the products had resulted from the polymerization of vinyl isocyanate as well as urea formation.

The instability of these materials, which was particularly enhanced during and after contact with ethanol, was probably due to the formation of the imine tautomer of the corresponding substituted urea. An ethanol adduct was believed to be intermediate in this tautomerism as follows:



(15)

Sato[30] has given a similar explanation of the increased instability of some N-1-alkenyl carbamates upon heating in the presence of alcohols.

The two compounds isolated from a solution of the impure N,N'-divinylurea in 95% ethanol are believed to be urea and the 2,4-dinitrophenylhydrazone of acetaldehyde. They caused no depression in melting points when mixed with

the authentic materials. Urea and acetaldehyde would be the expected products upon hydrolysis of the imine structure shown above and are consistent with the reactions of other N-1-alkenyl ureas.

Tests to determine the presence of trisubstituted biurets[73] in the above mixtures were negative.

A partially polymeric material has been prepared which is not cross-linked as evidenced by the determination of its solubility and melting point. The carbon, hydrogen and nitrogen content of this material agrees with the values calculated for N,N'-divinylurea. This material was unsaturated as shown by its ability to decolorize potassium permanganate. The fact that the total hydrogen uptake, during hydrogenation studies, was less than 50% of the theoretical amount for the di-unsaturated urea is an indication that reaction has occurred through both C=C double bonds. The intrinsic viscosity of this product was found to be 0.036 as compared to 0.017 for N,N'-diethylurea.* This difference in intrinsic viscosity of the two similar materials is an indication that the product of concern was polymeric. As another means of comparison, vinylurea has been polymerized by free radical initiation to give a product having an intrinsic viscosity of 0.034.[27]

*N,N'-diethylurea was obtained from the Pennsalt Chemical Corporation and recrystallized twice from ethanol.

A soluble, polymeric "divinylurea" has been prepared which showed no residual unsaturation in its infrared spectrum, whereas the starting material was highly unsaturated. The nitrogen content of this product was approximately 3% lower than the theoretical value for N,N'-divinylurea. The low nitrogen analysis might be justified if one assumed a low-molecular-weight polymer which contained end groups corresponding to the decomposed initiator. Assuming two fragments of dibenzoyl peroxide initiator per molecule of polymer and a degree of polymerization equal to ten, the calculated nitrogen content is 21.8%.

Acetone solutions of "N,N'-divinylurea" have been subjected to copolymerization with styrene to yield non-crystalline copolymers having intrinsic viscosities of 0.060 and 0.131. These products contained no residual unsaturation according to infrared analysis and hydrogenation studies.

The above results would certainly indicate that if N,N'-divinylurea is an intermediate in the formation of the polymeric products described, it reacts in such a way as to yield soluble polymers and copolymers that contain no residual unsaturation. It is therefore postulated that polymerization has taken place by the intramolecular-intermolecular chain propagation mechanism[58] to form

polymers containing cyclic units. It would be quite presumptuous on the part of the author, however, to make any definite conclusions concerning such properties of N,N'-divinylurea until the monomer has been isolated in a pure state.

Future preparations of N,N'-divinylurea by this same method should be carried out in the presence of a polymerization inhibitor in highly dilute solutions of vinyl isocyanate. A solvent in which the urea is expected to be insoluble should be used. Polymerizations and copolymerizations should be attempted in other systems as well as those which are free-radical initiated.

CHAPTER VI

SUMMARY

Three unsaturated isocyanates have been prepared by means of the Curtius rearrangement. Each has been investigated with respect to its reactivity as an isocyanate as well as an olefinic compound. The preparation of 9-decenyl isocyanate and β-allyloxyethyl isocyanate and the subsequent reactions of these compounds have heretofore been unreported in the literature. These longer chain compounds exhibited the classical reactions characteristic of saturated isocyanates with no complications. The reactions and resulting products of vinyl isocyanates were consistent with those previously reported.

Vinyl isocyanate was readily reactive as a monomer in free radical polymerizations, and such reactions were found to be difficult to control. The 9-decenyl and β-allyloxyethyl isocyanates could not be homopolymerized but could be copolymerized with vinyl and vinylidene compounds to give high-molecular-weight products which contained reactive isocyanate groups.

It was observed that cross-linked products could be obtained by copolymerization of each of the unsaturated

monomers, seemingly in the absence of added cross-linking reagents. This phenomenon is believed to result directly from the reactions of both the alkenyl and isocyanate functions within the monomers. Some evidence has been presented to support a postulation that the isocyanate reaction is one not unlike those in which such compounds form dimers and trimers.

Linear copolymers have also been prepared by reaction of each of the unsaturated isocyanates with vinyl and vinylidene monomers. These were then caused to react with mono- and difunctional active hydrogen-containing compounds to yield, respectively, linear and cross-linked polyureas and polyurethanes which exhibited properties different from the parent compounds.

A derivative of vinyl isocyanate, N,N'-divinylurea, is believed to be an intermediate in the formation of soluble polymers and copolymers. In view of the physical properties of the latter, it is suggested that they were formed by the intramolecular-intermolecular chain propagation mechanism.[59]

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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